M14/4/CHEMI/HP2/ENG/TZ1/XX/M

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MARKSCHEME

May 2014

CHEMISTRY

Higher Level

Paper 2

15 pages

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Subject Details: Chemistry HL Paper 2 Markscheme

Mark Allocation

Candidates are required to answer **ALL** questions in Section A **[40 marks]** and **TWO** questions in Section B **[2 x 25 marks]**. Maximum total = **[90 marks]**.

1. A markscheme often has more marking points than the total allows. This is intentional.

2. Each marking point has a separate line and the end is shown by means of a semicolon (;).

3. An alternative answer or wording is indicated in the markscheme by a slash (/). Either wording can be accepted.

4. Words in brackets ( ) in the markscheme are not necessary to gain the mark.

5. Words that are underlined are essential for the mark.

6. The order of marking points does not have to be as in the markscheme, unless stated otherwise.

7. If the candidate's answer has the same "meaning" or can be clearly interpreted as being of equivalent significance, detail and validity as that in the markscheme then award the mark. Where this point is considered to be particularly relevant in a question it is emphasized by ***OWTTE*** (or words to that effect).

8. Remember that many candidates are writing in a second language. Effective communication is more important than grammatical accuracy.

9. Occasionally, a part of a question may require an answer that is required for subsequent marking points. If an error is made in the first marking point then it should be penalized. However, if the incorrect answer is used correctly in subsequent marking points then **follow through** marks should be awarded. When marking, indicate this by adding **ECF** (error carried forward) on the script.

10. Do **not** penalize candidates for errors in units or significant figures, **unless** it is specifically referred to in the markscheme.

11. If a question specifically asks for the name of a substance, do not award a mark for a correct formula unless directed otherwise in the markscheme, similarly, if the formula is specifically asked for, unless directed otherwise in the markscheme do not award a mark for a correct name.

12. If a question asks for an equation for a reaction, a balanced symbol equation is usually expected, do not award a mark for a word equation or an unbalanced equation unless directed otherwise in the markscheme.

13. Ignore missing or incorrect state symbols in an equation unless directed otherwise in the markscheme.

SECTION A

1. (a) (i) $n(\mathrm{MgSO_4}) = \left(\frac{3.01}{120.37} = \right) 0.0250\,(\mathrm{mol})$; ***[1]***

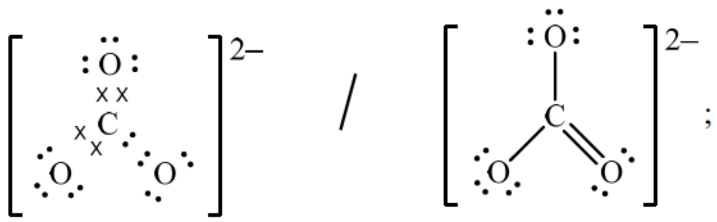
(ii) energy released $= 50.0 \times 4.18 \times 9.7 = 2027\,(\mathrm{J}) / 2.027\,(\mathrm{kJ})$;
$\Delta H_1 = -81\,(\mathrm{kJ\,mol^{-1}})$; ***[2]***
*Award **[2]** for correct answer.*
*Award **[2]** if 53.01 is used giving an answer of –86 (kJ mol^{-1}).*
*Award **[1 max]** for +81/81/+86/86 (kJ mol^{-1}).*
*Award **[1 max]** for –81000/–86000 if units are stated as J mol^{-1}.*
Allow answers to 3 significant figures.

(b) (i) $\Delta H\,(=\Delta H_1 - \Delta H_2) = -99\,(\mathrm{kJ\,mol^{-1}})$; ***[1]***
*Award **[1]** if –86 is used giving an answer of –104 (kJ mol^{-1}).*

(ii) $\frac{(103-99)}{103} \times 100 = 3.9\,\%$; ***[1]***
Accept answer of 2.9% if –100 used but only if a value for (b)(i) is not present.
*Award **[1]** if –104 is used giving an answer of 1.0%.*
Accept correct answers which are not to 1 decimal place.

(c) $MgSO_4$ not completely anhydrous / *OWTTE*;
$MgSO_4$ is impure;
heat loss to the atmosphere/surroundings;
specific heat capacity of solution is taken as that of pure water;
experiment was done once only so it is not scientific;
density of solution is taken to be 1 g cm^{-3};
mass of $7H_2O$ ignored in calculation;
uncertainty of thermometer is high so temperature change is unreliable;
literature values are carried out under standard conditions, but this experiment is not;
all solid not dissolved; ***[2 max]***

(d) (i) $H_2SO_4(aq) + MgCO_3(s) \rightarrow MgSO_4(aq) + CO_2(g) + H_2O(l)$; ***[1]***
Ignore state symbols.
Do not accept H_2CO_3.

(ii) 

Accept crosses, lines or dots as electron pairs.
Accept any correct resonance structure.
*Award **[0]** if structure is drawn without brackets and charge.*
*Award **[0]** if lone pairs not shown on O atoms.*

shape: trigonal/triangular planar;

bond angle: 120°;

Accept answers trigonal/triangular planar and 120° if M1 incorrect, but no other answers should be given credit. ***[3]***

(iii) (pi/π) electrons are delocalized/spread over more than two nuclei / charge spread (equally) over all three oxygens; ***[1]***

(iv) sp^2; ***[1]***

2. (a) experiments 1 and 2 ([$S_2O_3^{2-}$] remains constant) change in [H^+] does not affect the rate so zero order with respect to H^+(aq) / *OWTTE*;
experiment 1/2 and 3 ([H^+] has no effect) [$S_2O_3^{2-}$] is halved and rate is also halved so first order with respect to [$S_2O_3^{2-}$] / *OWTTE*; ***[2]***
Accept explanation given in mathematical terms.
*Award **[1 max]** if both [$S_2O_3^{2-}$] is first order, **and** [H^+] is zero order are stated without reason.*

(b) rate $= k[S_2O_3^{2-}]$; ***[1]***

(c) 0.18;
s^{-1}; ***[2]***

(d) $S_2O_3^{2-} \rightarrow S + SO_3^{2-}$; ***[1]***
Accept any balanced equation that starts with only one $S_2O_3^{2-}$.
Equations must be balanced in terms of number of atoms and charge.

(e) determine rate at a range of temperatures (while keeping concentrations constant);
calculate k for each temperature;
plot graph of ln k against T^{-1};
gradient is $\frac{-E_a}{R}$ /*OWTTE*; ***[3 max]***

3. (a) *Q:* creates positive ions/cations / electron is knocked off atom / *OWTTE*;
by bombardment of electrons;

S: ions deflected by an (external) magnetic field;
deflection of ions depend on mass/m/z (and charge) / heavier ions are deflected less than lighter ions / more highly charged ions are deflected more than less highly charged ions; ***[4]***
*Award **[1 max]** for simply stating ionization and deflection.*

(b) $(A_r =) 0.7899 \times 24 + 0.1000 \times 25 + 0.1101 \times 26$;
24.32; ***[2]***
*Award **[2]** for correct final answer.*
*Award **[1 max]** for 24.31 with correct working.*
*Award **[0]** for 24.31 (Data Booklet value) if working is incorrect or no working is shown.*
*Final answer must be to 2 decimal places to score **[2]**.*

4. (a) heat /warm/ 140 – 225 °C ;
Do not accept high temperature.
(finely divided) catalyst / Zn/Cu/Ni/Pd/Pt; ***[2]***

(b) $\Delta H^{\ominus} = \left(\Sigma\Delta H_f^{\ominus}(\text{products}) - \Sigma\Delta H_f^{\ominus}(\text{reactants}) = -127 - (110 + 0) = \right) - 237\,(\text{kJ mol}^{-1})$; ***[1]***

(c) $\Delta G^{\ominus} = \left(\Sigma\Delta G_f^{\ominus}(\text{products}) - \Sigma\Delta G_f^{\ominus}(\text{reactants}) = -16 - (152 + 0) = \right) - 168\,(\text{kJ mol}^{-1})$; ***[1]***

(d) (i) $\Delta S^{\ominus} = \left(\dfrac{\Delta H^{\ominus} - \Delta G^{\ominus}}{T} = \right)\dfrac{-237 - (-168)}{298}$;

$= -0.232\,(\text{kJ}\,K^{-1}\,\text{mol}^{-1})$; ***[2]***
*Award **[2]** for correct final answer.*
*Award **[2]** for –232 $J\,K^{-1}\,mol^{-1}$ (units must be given).*

(ii) 3 mol of gaseous reactants and 1 mol of gaseous products / fewer moles of gas in products; ***[1]***

(iii) spontaneity decreases (as temperature increases because $T\Delta S^{\ominus}$ becomes a larger negative value/ $\Delta G^{\ominus}$ becomes positive at higher temperatures); ***[1]***

(iv) $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} = 0 \,/\, -237 - T(-0.232) = 0$;
$T = 1020\,(K)$;
Remember to allow ECF from 4(d)(i). ***[2]***

(v) $\Delta S^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants}) \;/\; -232 = 310 - (279 + 2S^{\ominus}(\text{H}_2))$;
$S^{\ominus}(\text{H}_2) = \tfrac{1}{2}(310 - 279 + 232) = 132\,\text{J K}^{-1}\,\text{mol}^{-1}$; ***[2]***
*Award **[2]** for correct final answer.*
Remember to allow ECF from 4(d)(i).

SECTION B

5. (a) (i) basic to acidic;
$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$;
$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$; ***[3]***
Ignore state symbols.

(ii) molten Al_2Cl_6 does not conduct electricity **and** molten Al_2O_3 does;
Al_2Cl_6 is a covalent molecule **and** has no free charged particles to conduct electricity;
Al_2O_3 is ionic/has ions which are free to move when molten; ***[3]***

(iii) $Cl_2(g) + H_2O(l) \rightleftharpoons HCl(aq) + HClO(aq)$; ***[1]***
Ignore state symbols.
Allow $\rightarrow$.

(b) (i) $Br_2(aq)$: no change;
KBr (aq): colour change / from colourless to red/yellow/orange/brown; ***[2]***

(ii) $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$;
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$; ***[2]***
Ignore state symbols.
Accept e instead of e^-.

(c) (i) HF has hydrogen bonds (between molecules); ***[1]***

(ii) strength of van der Waals'/London/dispersion forces increases;
as mass/size/number of electrons of halogen atom/molecule increases; ***[2]***

(d) (i) *Cr:* $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ / $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$;
Cr^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$; ***[2]***

(ii) H_2O is a ligand / has lone (electron) pair;
forms dative (covalent)/coordinate bond / donates a lone (electron) pair ;
ligand is Lewis base / Cr^{3+} is Lewis acid; ***[3]***

(iii) Cr^{3+} has partially filled d orbitals;
d orbitals split into two levels / three lower energy and two higher energy levels;
energy difference is in visible part of spectrum;
electrons absorb visible light / one colour/frequency/wavelength;
electron transitions occur from lower to higher energy level within d sub-level;
complementary colour/colour not absorbed is seen; ***[3 max]***

(iv) acidic because $[Cr(H_2O)_6]^{3+}(aq) \rightarrow [Cr(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$; ***[1]***
Allow answers with further equations.
Accept any other valid equations.
Ignore state symbols.

(e) successive ionization energy values increase with removal of each electron;
large increase in ionization energy when sixth electron is removed;
as electron is one energy level/shell closer to the nucleus; ***[2 max]***
Accept a suitably annotated diagram.

6. (a) (i) $C_4H_9OH(l) \rightarrow C_4H_8O(l) + 2H^+(aq) + 2e^-$; ***[1]***
Ignore state symbols.

(ii) $3C_4H_9OH(l) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3C_4H_8O(l) + 2Cr^{3+}(aq) + 7H_2O(l)$; ***[1]***
Ignore state symbols.

(iii) $CH_3CH_2CH_2CH_2OH$;
$(CH_3)_2CHCH_2OH$;
Accept full or condensed structural formulas. ***[2]***

(iv) $(CH_3)_3COH$;
2-methylpropan-2-ol;
Allow 2-methyl-2-propanol, methylpropan-2-ol, methyl-2-propanol.

tertiary; ***[3]***

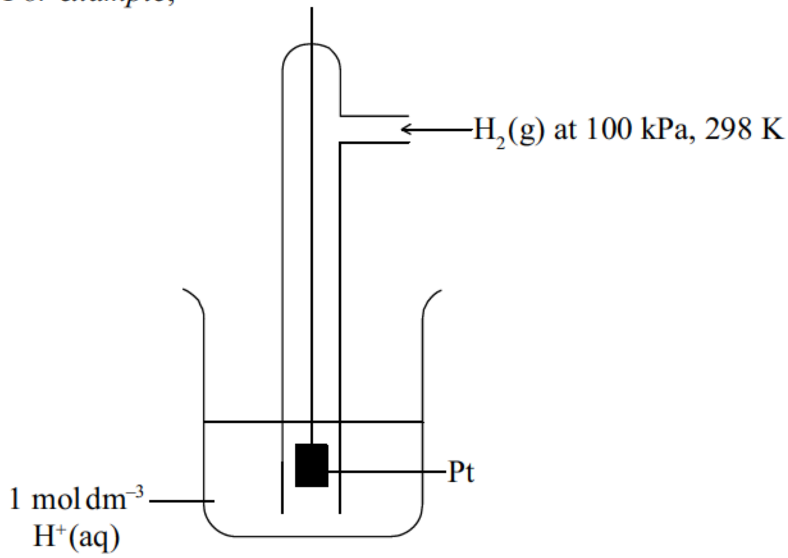
(v) $C_4H_9OH + 6O_2 \rightarrow 4CO_2 + 5H_2O$ / $(CH_3)_3COH + 6O_2 \rightarrow 4CO_2 + 5H_2O$
correct reactants and products;
correct balancing; ***[2]***

(b) (i) $Z < W < X < Y$;
Accept $Y > X > W > Z$. ***[1]***

(ii) $X(s) + Z^{2+}(aq) \rightarrow X^{2+}(aq) + Z(s)$; ***[1]***
Ignore state symbols.
Accept $X(s) + ZCl_2(aq) \rightarrow XCl_2(aq) + Z(s)$.

(iii) $H_2(g)$/hydrogen; ***[1]***

(iv) diagram showing gas, solution and solid electrode;
For example,



This diagram scores ***[3]****.*

$1\ mol\ dm^{-3}\ H^+(aq)$ **and** Pt;
Allow 1 mol L^{-1} or 1 M.
Allow 1 mol dm^{-3} HCl (aq) or other source of 1 mol dm^{-3} H$^+$(aq) ions.

100 kPa/10^5 Pa/1 bar ($H_2(g)$ pressure) **and** 298 K / 25 °C; ***[3]***
Ignore state symbols throughout.
Allow 1.01×10^5 Pa/1 atm.

(c) (i) *Positive electrode (anode):*
$I^-(aq) \rightarrow \frac{1}{2}I_2(aq) + e^-$;
Accept correct equation involving 2 mols of I^-.

Negative electrode (cathode):
$H_2O(l) + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-(aq)$ / $H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$ /
$H_3O^+(aq) + e^- \rightarrow H_2O(l) + \frac{1}{2}H_2(g)$; ***[2]***
Award ***[1 max]*** *if correct equations are given at the wrong electrodes.*
Ignore state symbols.
Allow e instead of e$^-$.
Penalize equilibrium sign once only.
Accept correct equation involving 2 mols of H$^+$.

(ii) aluminium will be oxidized (instead of I^-) at positive electrode (anode);
aluminium is a reactive metal / oxidation of aluminium has a positive $E^{\ominus}$ /
aluminium is higher on the reactivity series than I^- / *OWTTE*; ***[2]***

(d) (i) $n_{Sn} = n_{Cu} = 2.86 \times 10^{-4}$ / 0.000286 (mol);
$m(Cu) = 2.86 \times 10^{-4} \times 63.55 = 0.0182$ (g); ***[2]***

(ii) blue colour persists in second cell **and** fades in third cell;
pH does not change in second cell **and** decreases in third cell; ***[2]***
*Award **[1 max]** if both colour and pH are correctly stated for one only of either second or third cell.*

(iii) *Colour:*
positive Cu electrode (anode) is oxidized to maintain colour in second cell /
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$;

pH:
in third cell, H^+ ions are produced as water is oxidized at positive electrode (anode) / $H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$ / solution becomes acidic as hydroxide ions are oxidized at positive electrode (anode) /
$2OH^-(aq) \rightarrow \frac{1}{2}O_2(g) + H_2O(l) + 2e^-$; ***[2]***
Ignore state symbols.

7. (a) (i) $(K_c =)\dfrac{[Cl_2(g)][NO(g)]^2}{[NOCl(g)]^2}$; *[1]*

Ignore state symbols.

(ii) equilibrium shifts to right as there are more moles (of gas) on product side;
no change to K_c as it is a constant at fixed temperature / *OWTTE*; *[2]*

(iii) $[NOCl(g)] = 1.80\,(mol\,dm^{-3})$;
$[Cl_2(g)] = 0.100\,(mol\,dm^{-3})$;
$K_c = \left(\dfrac{0.100 \times (0.200)^2}{(1.80)^2} = \right) 1.23 \times 10^{-3}\,(mol\,dm^{-3})$; *[3]*

*Award **[3]** for correct final answer.*

(iv) exothermic as K_c is lower at higher temperature; *[1]*

(b) (i) hexane has lower boiling point **and** enthalpy of vaporization than pentan-1-ol / *OWTTE*;
hexane has higher vapour pressure than pentan-1-ol / *OWTTE*; *[2]*

(ii) hexane is non-polar / has only van der Waals'/London/dispersion forces / has weaker intermolecular forces than pentan-1-ol;
pentan-1-ol has hydrogen bonding between molecules; *[2]*

(c) (i) $[OH^-] = \sqrt{1.50 \times 1.78 \times 10^{-5}} = 5.17 \times 10^{-3}\,(mol\,dm^{-3})$;
$pH = (14 - pOH = 14 - 2.29 =) 11.71$; *[2]*

*Award **[2]** for correct final answer.*
Accept correct answer with more than 2 decimal places.

(ii) solution which resists change in pH / changes pH slightly / *OWTTE*;
when <u>small</u> amounts of acid or base are added; *[2]*

(iii) $[NH_3] = \left(\dfrac{(1.50 \times 0.0200) - (0.500 \times 0.0250)}{0.0450} = \right) 0.389\,(\text{mol dm}^{-3})$;

$[NH_4^+] = \left(\dfrac{(0.500 \times 0.0250)}{0.0450} = \right) 0.278\,(\text{mol dm}^{-3})$;

$[OH^-] = \left(\dfrac{K_b[NH_3]}{[NH_4^+]} = \right) \dfrac{1.78 \times 10^{-5} \times 0.389}{0.278} = 2.49 \times 10^{-5}\,(\text{mol dm}^{-3})$;

$pH = (14.0 - pOH = 14.0 - 4.60 =) 9.40$;

OR

$pOH = pK_b + \log\dfrac{[NH_4^+]}{[NH_3]} = pK_b + \log\dfrac{(12.5/1000)}{(17.5/1000)}$;;

$pOH = 4.75 + \log\left(\dfrac{12.5}{17.5}\right) = 4.75 - 0.146 = 4.604$;

$pH = 14.0 - 4.604 = 9.40$; ***[4]***

*Award **[4]** for the correct final answer.*

(iv) $\left(V(NH_3) = \dfrac{25.0 \times 0.500}{1.50} = 8.33\,\text{cm}^3\right)$

$V = V(NH_3) + V(HCl) = 8.33 + 25.0 = 33.3\,\text{cm}^3 / 0.0333\,\text{dm}^3$; ***[1]***

(v) (NH_4^+ ions are present at equivalence point $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$ at equivalence $n(NH_4^+ \text{ produced}) = n(NH_3 \text{ added}) = n(HCl)$)

$[NH_4^+] = \dfrac{0.500 \times 0.0250}{0.0333} = 0.375\,(\text{mol dm}^{-3})$;

($NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq) / NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

$pK_a(NH_4^+) = 14 - pK_b(NH_3) = 14.00 - 4.75 = 9.25$)

$K_a = \dfrac{[NH_3(aq)][H^+(aq)]}{[NH_4^+(aq)]} = 5.62 \times 10^{-10}$;

$[H^+(aq)] = \sqrt{5.62 \times 10^{-10} \times 0.375} = 1.45 \times 10^{-5}\,(\text{mol dm}^{-3})$;

$pH = 4.84$; ***[4]***

*Award **[4]** for the correct final answer.*

(vi) bromocresol green / methyl red; ***[1]***

ECF for answer in 7(c)(v) if pH given is below 7.

8. (a) HCl is a strong acid **and** CH_3COOH is a weak acid so HCl has higher conductivity / HCl dissociates completely in water **and** CH_3COOH does not, so HCl has higher conductivity / HCl is a stronger acid (than CH_3COOH) so has higher $[H^+]$ and higher conductivity; ***[1]***

(b) (i) $CH_3COOH(aq) + HCO_3^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l) + CO_2(g)$; ***[1]***

Accept $NaHCO_3(aq)$ and $CH_3COONa(aq)$ instead of ions.
Ignore state symbols.

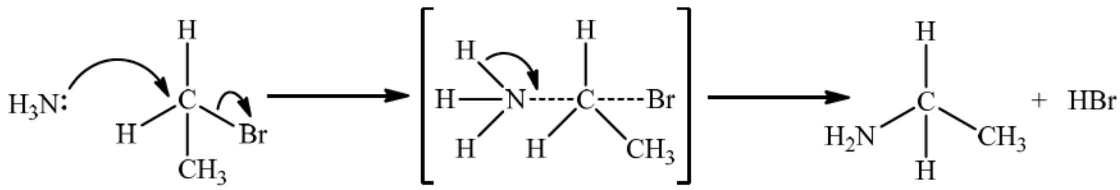
(ii) $n(CH_3COOH) = 0.00500(mol)$ **and** $n(NaHCO_3) = 0.00450(mol)$;
$NaHCO_3$ is limiting; ***[2]***

(iii) $n(CO_2) = n(NaHCO_3) = 0.00450(mol)$;
$m(CO_2) = 0.00450 \times 44.01 = 0.198(g)$; ***[2]***
*Award **[2]** for correct final answer.*

(c) (i) $T = 363K$ **and** $V = 9.50 \times 10^{-5}\ m^3$;
Accept $V = 9.5 \times 10^{-2}\ dm^3$ if P is used as 101 kPa in calculation.
$n = \frac{PV}{RT} = \frac{1.01 \times 10^5 \times 9.50 \times 10^{-5}}{8.31 \times 363}$;
$= 3.18 \times 10^{-3}(mol)$; ***[3]***
*Award **[3]** for correct final answer.*

(ii) $M = \left(\frac{m}{n} = \frac{0.348}{3.18 \times 10^{-3}} = \right) 109\ (g\ mol^{-1})$; ***[1]***

(d) (i)



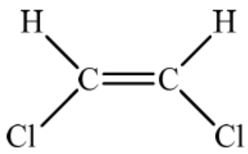
curly arrow going from lone pair on N in NH_3 to C;
curly arrow showing Br leaving;
Accept curly arrow going from bond between C and Br to Br on 1-bromoethane or on the transition state.

representation of transition state showing square brackets, two partial bonds **and** curly arrow going from NH bond to NC partial bond/curly arrow going from NH bond to N; ***[3]***
Do not penalize if NH_3 and Br are not at 180° to each other.
Do not award M3 if NH_3—C bond is represented.

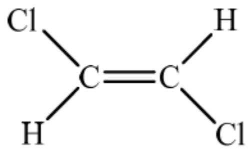
(ii) react CH_3I with CN^-/KCN solution to form ethanenitrile;
(reduce nitrile by heating with) H_2;
Ni (catalyst); ***[3]***

(iii) elimination;
NaOH /KOH dissolved in (hot) ethanol/alcohol;
heat /hot / reflux; *[3]*

(e) (i) compounds with same structural formula but different arrangements of atoms in space; *[1]*

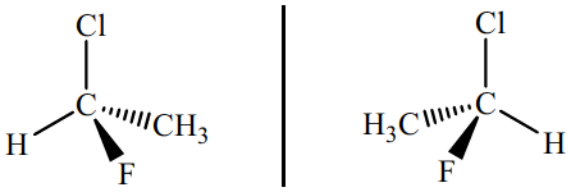
(ii) 

and



; *[1]*

(iii) restricted rotation around (C=C) double bond; *[1]*

(iv) 

; *[1]*

The two structures must be clear 3D representations of mirror images.
Tapered (wedge/dash) notation not necessary.

(v) the two enantiomers rotate the plane of plane-polarized light by equal amounts, but in opposite directions;
using a polarimeter; *[2]*